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TECHNICAL MEMORANDUM No. 2/M/50

Thermodynamic Functions of Fluorine and some of its compounds

EXCLUDED FROM GENERAL DECLASSIFICATION SCHEDULE EXECUTIVE ORDER 11652

N. W. Luft

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ARMY ATTACHE LONDON

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Thermodynamic Functions of Fluorine and some of its Compounds
ARMYAT-London
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1 John L. Atkins, Research Analyst E.R.D.E.

H. W. Luft is the author of Explosives Research and Development Establishment Tech. Memo No. 2/M/50. The Thermodynamic functions $-(F^o - H^o_0)/T$, S^o, C_p^o, log Kf^o in the temperature range from 300 to 2000°K. are given for the following molecules: - F, F_2, HF, ClF, BrF, BF, BeF, F_2O,

NF_3, PF_3, AsF_3, ClF_3, BF_3.

SiF_4, SF_6.

CF_4, COF_2, C_2F_6.

A series of important equilibrium constants have been calculated.

COMMENT: Fluorine and its dirivatives will be of interest to the Rocket and Jet Propulsion Sections of Ordnance Department. The U.S. Naval and Air Attaches, London, have received 5 copies each of this publication. One copy for R&D Board.

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TECHNICAL MEMORANDUM 2/M/50

Thermodynamic Functions of Fluorine and Some of its Compounds

By

N.W. Luft

This memorandum contains no classified information of overseas origin.

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CONTENTS

Reference: XR 880/2

I. SUMMARY.

The thermodynamic functions $-(F^o - H^o_0)/T$, S^o, $C_p{}^o$, log Kf^o in the temperature range from 300 to 2000°K. are given for the following molecules:-

F, F_2, HF, ClF, BrF, BF, BeF, F_2O,

NF_3, PF_3, AsF_3, ClF_3, BF_3,

SiF_4, SF_6,

CF_4, COF_2, C_2F_6.

A series of important equilibrium constants have been calculated.

II. NOTATION.

r_0 = nuclear separation, bond length (in the zero vibrational level), ($A = 10^{-8}$ cm.).

B = rotational constant (cm^{-1}).

I = moment of inertia (10^{40}. $g.cm^2$).

ω = vibrational frequency (cm^{-1}). In polyatmoic molecules the degeneracy is added in brackets.

$x\omega$ = anharmonicity constant (cm^{-1}).

v = vibrational quantum number.

ν = value of electronic term (cm^{-1}).

s = symmetry number.

M = molecular weight.

P_E = statistical weight of electronic state.

μ = dipole moment (Debye Unit = 10^{-18} e.s.u.).

P = (partial) pressure (atm.).

$(F) \equiv -(F^o-H^o_0)/T$ = free energy function.

S^o = (virtual) entropy, not containing contributions from nuclear spin (S_N) and isotope mixing (S_{mix}).

C^o_p = molar heat capacity.

ΔH = enthalpy of reaction.

ΔHf^{o} = enthalpy of formation from elements in their standard states.

D = dissociation energy.

K_p = equilibrium constant.

Kf = equilibrium constant of formation.

R = universal gas constant.

T = temperature (°K.).

III. INTRODUCTION.

Recently the chemistry of fluorine compounds has become the object of increased interest (1,2,3), mainly because of the possible technical applications of such compounds. The thermodynamic functions of certain fluorine compounds have therefore been calculated and from these, equilibrium data for various reactions of technical interest have been obtained.

Some of these data are taken from the literature. Additional data have been calculated from spectroscopic results by well-known statistical methods (4,5,49).

As the main interest lies in the region below 2000 or even 1500°K. it has been thought sufficient to use the model of the harmonic oscillator and rigid rotator ('HORR-approximation') in these calculations for molecules in the perfect gas state. Vibrational contributions were calculated from Wilson's tables (cf.4).

IV. SPECTROSCOPIC, MOLECULAR AND THERMOCHEMICAL DATA.

The practical limit to the accuracy of the calculated figures is set by the accuracy of available spectroscopic, molecular and thermochemical data. These data are reviewed in the following sections; thus an estimate of the accuracy of the thermodynamic functions in the appendix is easily possible.

1. Atomic fluorine, F.

Apart from the ground state $^2P_{3/2}$ with $p_{E0} = 4$, the first excited state $^2P_{1/2}$ at $\nu_{E1} = 407$ cm^{-1} is also taken into account. The $^4P_{5/2}$ state has no influence below T = 4000°K.

Murphy and Vance (7) represent the free energy function of atomic fluorine by the formula:-

$$-(F^o - H^o_o)/T = a/T + b\log T + cT + dT^2 + i$$

with $a = -754.75$, $b = 4.6445$, $c = 40.38 \times 10^{-4}$, $d = -74.70 \times 10^{-8}$

$i = 22.5832.$

This formula gives satisfactory results up to about 2000°K. which agree closely with the figures of Table I. The contribution $S_N = 1.377$ for nuclear spin $\frac{1}{2}$ is not included in these figures.

Equilibrium constants of formation of atomic fluorine according to the equation

$$\tfrac{1}{2}F_2 \rightarrow F$$

have been calculated with the enthalpies of formation ΔHf^o_o (F) = +20 and +16.2 k.cals. (see below).

2. Fluorine, F_2.

The ground state is $^1\Sigma$, point group $D_{\infty h}$ $P_{EO} = 1$, $s = 2$. Electron diffraction measurements (8) give the nuclear equilibrium distance $r_e(F\text{-}F) = 1.435 \pm 0.01$; from this, $r_o = 1.45$ is assumed; this gives a moment of inertia of $I_o = 33.16$ in fair agreement with (7).

Apart from less reliable data e.g. Born-Haber cycles for the lattice energy of fluorides according to Meyer-Helmholtz, there has been recent experimental evidence (9) for a low value of the dissociation energy of F_2 viz:-

$$D(F_2) \equiv 2\Delta Hf^o_o(F) = +32.4 \text{ k.cals.}$$

from a spectroscopic determination of D(FCl) and a value of $\Delta Hf(FCl)$ = -15.0 k.cals. A second new value $\Delta Hf(FCl)$ = -11.6 k.cals. (ref.20) gives $D_o(F_2)$ = +39.5 k.cals.

A low value of this order is supported by various thermochemical arguments, cf. (6), (26). Equilibrium constants Kf^o for the formation of atomic fluorine F are given in the appendix with the two values $Hf^o_o(F)$ = 16.2 and ~20 k.cals., since the previous value $D(F_2)$ ~63 k.cals. is not supported by direct measurement.

The vibrational frequency of F_2 in the ground state is not known for certain. Together with unknown upper states it may be the main source of error. Gale and Monk (10), who could not detect a limit of convergence in absorption as far as λ4100Å (~69 k.cals.), made an analysis of F_2 bands between λ5100 Å and λ7200Å in emission. Structure and intensities indicate a $^1\Sigma - \Pi$ transition with

$$\nu = 17438.8 + (1104.9v' - 2.9v'^2) - (1071.5v'' - 9.9v''^2)$$

$$I'_o = 34.2;\ r'_o = 1.48;\ I''_o = 26.0;\ r''_o = 1.28$$

/Although

Although this system probably involves only upper states and shows perturbation, both vibrational frequencies have been wrongly used at times for the ground state of F_2 (cf. 11).

Murphy and Vance (7) derived an approximate value of ω_o by means of Badger's rule (12). With the old value $r_e = 1.45$ they obtain $\omega_o = 856\ cm^{-1}$, whereas the new $r_e = 1.435$ gives $\omega_o = 892$ and $1062\ cm^{-1}$ from the rules for rows and columns of the periodic table respectively (cf. 8). From a comparison of the vibrational frequencies for I_2, Br_2, Cl_2 (cf. 14, 15) in the ground state $^1\Sigma^+_g$ and 8 stable upper states:-

$$^3\Pi_{1u};\ ^3\Pi^+_{0g};\ ^3\Pi^+_u;\ ^3\Sigma^+_u;\ ^3\Pi_{1g};\ ^1\Sigma^+_u;\ \Pi_{21g};\ ^1\Pi_g$$

one finds that Π_{21g} is the only upper state in which ω_o is greater than in the ground state, and $r_e^n(\sim 1/\omega_e)$ smaller. If this is also true for F_2 then Gale and Monk's spectroscopic results indicate that in the ground state of F_2 the vibrational frequency is not smaller than $\omega \sim 1070\ cm^{-1}$.

Owing to the lack of data this frequency $\omega_o = 1070$, supported by the above result from Badger's rule, is used in the following calculations.* $\omega \sim 1130$ quoted in (11) would cause only a minor difference.

From any of these values of ω_o and the low value of $D(F_2)$ a high anharmonicity $x_e\ \omega_e$ must be expected; this is in agreement with an argument by Walsh (13) on possible repulsion between bonding and other orbitals in molecules made up of small and highly electro-negative atoms. An approximate value for $x_e\omega_e$ can be derived by applying the rule (14).

$$m^* x_e \omega_e r_e^n = \text{const.} \qquad m^* = \text{reduced mass}$$

in the series of halogens, viz. $x_e\ \omega_e \sim 20\ cm^{-1}$. Linear extrapolation of vibrational levels to their convergence limit (45):-

$$D_o = \frac{\omega_e^2}{4\ x_e\omega_e} - \tfrac{1}{2}\omega_e$$

which gives too large values for I_2 and Br_2, but only slightly too low for Cl_2, yields $D_o(F_2) \lesssim 40$ k.cals. in agreement with the values given above.

No anharmonicity nor upper electronic states are taken into account

/although

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* Recently (43) a Raman shift $\omega = 892.1 \pm 2\ cm^{-1}$ has been found in F_2 and accepted as its fundamental frequency. This gives $\omega_o \sim 920\ cm^{-1}$ and results in thermodynamic functions which are intermediate between those of ref.(7) and the present values of Table I.

although the levels and structures of the first excited states of F_2 may differ from those of the other halogens.

3. Hydrogen fluoride, HF.

The molecular ground state is $^1\Sigma_g^+$. Upper states which must be high are not known. For molecular and spectroscopic data (cf. 15) $\omega_o = 4050.4$, $x_e\omega_e = 90.9$; $B_o = 20.542$ giving $r_o = 0.917$ and $I_o = 1.362$.

The thermodynamic functions are those by Murphy and Vance (7) with slight corrections for the new values of the universal constants.

Equilibrium constants Kf^o have been calculated with the new value (17, 27) $\Delta Hf_0^o(HF) = -64.5$ k.cals. With the new $D(F_2) = 40$ or 32.4 k.cals. this corresponds to $D(HF) = 136.1$ or 132.3 k.cals. and to the electronegativity differences (24) $X_{HF} = D(HF) - [D(H_2).D(F_2)]^{\frac{1}{2}} = 72.7$ or 75.3 k.cals. in agreement with the high dipole moment $\mu = 1.91$.

4. Chlorine mono fluoride, ClF.

Wahrhaftig (19) and, more recently, Schmitz and Schumacher (9) have analysed the absorption spectrum. The ground state is $^1\Sigma_g^+$ and a perturbation of the vibrational levels is explained as pre-dissociation (limit ~60.8 k.cals.). By comparison with ICl and IBr spectra, Wahrhaftig concludes that the upper state is $^3\Pi_0^+$. The vibrational analysis of (9), (19) is based upon the three most distinct bands at ~21000cm^{-1} and including subsequent diffuse bands, the convergence limit is obtained at 21500 cm^{-1} (~61.4 k.cals.). The state of the F atoms formed in dissociation has not been established; but if we assume that the F-atoms are excited ($^2P_{1/2} = 1.1$ k.cals.) the dissociation energy of ClF into normal atoms is $D(FCl) = 60.3$ k.cals.

It might be that the band system actually involves transitions from the $v'' = 1$ ground state level instead of the $v'' = o$, and this cannot definitely be excluded by applying the Franck-Condon principle to Morse-curves constructed from the known data. In the case of $v'' = 1$ the value of $D_o(ClF)$ would be increased by 2.3 k.cals.; altogether, D(FCl) would not be higher than 64 k.cals. and $D(F_2)$ not higher than 45 k.cals. Compared with the available experimental evidence, Wicke's (58) recent argument in favour of $D(F_2) = 63$ k.cals. is not convincing.[x] The data for the two states of ClF is:-

x $^1\Sigma_g^+$: $B_e = 0.518$; $\alpha_e = 0.006$; $\omega_e = 793.2\ (780.4)$; $x_e\omega_e = 9.9\ (4.0)$;

$r_e = 1.625$; $\omega_o = 783\ (776)$; $r_o = 1.630$; $I_o = 54.35$

A $^3\Pi_0^+$ $B_e = 0.327$; $\alpha_e = 0.014$; $\omega_e = 313.5\ (316.4)$; $x_e\omega_e = 2.22\ (11.8)$;

$r_e = 1.92$; $\omega_o = 311\ (305)$; $r_o = 1.93$;

/Values

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x Recent infra red and Raman studies (62) confirm the above frequency of the ground state of ClF and therefore support the value D(FCl) = 60.3 k.cals.

Values in brackets are from (9). The micro-wave spectrum of FCl (28) agrees excellently with Wahrhaftig's rotational analysis. Wells (56) calculated r(FCl) = 1.62 from Shomaker & Stevenson's (59) law for bond lengths. The dipole moment (28) is $\mu = 0.88$ in agreement with a certain amount of ionic contribution to the bond energy, $x_{FCl} = D(FCl) - [D(F_2).D(Cl_2)]^{\frac{1}{2}}$ 15 k.cals.

Thermodynamic data have been calculated by Potter (29) in the HORR approximation up to 2000°K. from Wahrhaftig's data with corrections for the isotopy of Cl. These data are given in the appendix; they do not contain the mixing term for isotopy $S_{mix} = 1.109$. The $^3\Pi$ state has been neglected since, even at 2000°K. it has only a minor influence on the thermodynamic functions. The correction for isotopy is of a bigger order but still small.

Equilibrium constants Kf have been calculated with the two values

$$\Delta Hf^{o}_{300} \text{(FCl)} = -11.6 \text{ and } -15.0 \text{ k.cals.} = \Delta Hf^{o}_{o} \text{(FCl)}$$

according to (20) and (9) respectively, since a decision between these two values is not possible at the moment. Perhaps a comparison of the two theoretical temperatures in the reaction $Cl_2 + F_2 \rightarrow 2ClF$, corresponding to the alternative values ΔHf^o_o(FCl), with an experimentally determined one, could settle the dispute. A third value $\Delta Hf^o_{300} = -13.9$ k.cals. is obtained by the combination of ΔHf(NaF) = -138.2 and ΔHf(NaCl) = -99.8 k.cals.(55) with the enthalpy change $\Delta H = -24.5$ k.cals.(9) for the reaction

$$NaCl + ClF \rightarrow NaF + Cl_2$$

At the time of this investigation Ward and Hussey (57) published thermodynamic functions of FCl from 2000 up to 5000°K. calculated with $\omega_o = 773$, $I_o = 54.35$ by the HORR approximation, and, including the $^3\Pi$ state ($P_{El} = 6$). Their equilibrium constants are based on ΔHf^o_o(FCl) = -15.0 k.cals.

5. Bromine fluoride, BrF.

Vibrational analysis (25) gives $\omega_o = 665$ and $X_o\omega_o = 3$ for the $^1\Sigma^+_g$ ground state. As a rotational analysis has not been made, the value r_o = 1.85 is used, calculated from bond radii (24) * which gives a moment of inertia $I_o = 87.23$.

The thermodynamic functions in the appendix do not include upper states, correction for the anharmonicity of vibration or the effect of isotope mixing. The error thus incurred is probably not serious.

/The

* A recent micro-wave analysis (63) gives $r_e = 1.759$ and $I_e = 78.355$ for $Br^{79}F$. This corresponds to $I_o = 79.0$ and requires a reduction of the values for S and (F) in Table I by 0.199 units.

The energy of dissociation is D(BrF) = 50.3 or 59.9 k.cals.(25) depending on whether F or Br is the excited one of the dissociation product. If we discard the second value, then, according to the value of $D(F_2)$ chosen, we obtain ΔHf^o_o (BrF) = -7.6 or -11.4 k.cals. The first value, corresponding to $D(F_2)$ = 40 k.cals. has been used in calculating the equilibrium constants of formation.

6. Boron mono-fluoride, BF.

The ground state is $^1\Sigma$ (44) in contrast to the earlier assignment $^3\Pi$ (15), therefore $P_{EO} = 1$, S = 1.

r_o(B-F) = 1.30 is used (50), whereas r_o(B-F) is equal to 1.29 in BF_3 and = 1.32 in BF in the hypothetical $^3\Pi$ state; thus $I_o = 19.34$.

Bibliography (44) gives also $\omega_o = 1400$, instead of the previous value of 1314 and $\omega_o X_o = 12$. The first excited state is at 51083 cm^{-1} (~147 k.cals.) so that it need not be taken into account below 4000°K.

The previous value (45) of the bond energy D(BF) ~105 k.cals. is probably incorrect. Linear Birge-Sponer extrapolation gives ~140 k.cals. which is also the order of the average dissociation energy of BF bonds in BF_3. The enthalpy of formation is

$$\Delta Hf^o_o(BF) = \Delta Hf^o_o(F) + \Delta Hf^o_o\,(B_{gas}) - D(BF) \;\; \sim 115 - D(BF) \;\; \sim -25 \text{ k.cals.}$$

whereas (18) gives -18 k.cals.; the former value is used in the calculation of equilibrium constants. The values of the thermodynamic functions of BF are given in the Appendix; they do not include the mixing term $S_{mix} = 0.989$ and the influence of isotopy on I and ω is omitted since this data is not of high accuracy. The thermodynamic functions of BF, which are put forward by Ward and Hussey (57) for the temperature ranges 300-2000°K. and 2000 - 5000°K. respectively are incorrect since they imply a $^3\Pi$ ground state.

7. Beryllium-monofluoride, BeF.

Molecular data (11,15,52): $^2\Sigma$, $C_{\infty v}$ $P_{EO} = 1$, S = 1, r_o(BeF) = 1.35, $\omega_o = 1256.5$, $I_o = 18.70$.

Hf^o_o(BeF) is not known, D(BeF) is very uncertain. Linear Birge-Sponer extrapolation of vibrational data gives D(BeF) = 102, whereas Herzberg (15) records ~125 k.cals. From thermochemical data and average bond energies in BeF_2 the value D(BeF) ~145 k.cals. is obtained as an upper limit. It may be that the first bond in BeF_2 is stronger that the second one (cf.54) so that Herzberg's figure would be of the right order. In view of this uncertainty no values of Kf^o have been calculated.

8. Fluorine monoxide, F_2O.

The thermodynamic functions given in Appendix are those calculated by Potter (29) with the molecular data:-

$^{1}\Sigma$, C_{2v}, $P_{EO} = 1$, $S = 2$, $\omega_o = 833,\ 492,\ 1110\ cm^{-1}$, $r_o(F\text{-}O)$
$= 1.41 \pm 0.05 \mathring{A}$, angle $F\hat{O}F = 100 \pm 5^{\circ}$, $I_A = I_B + I_c = 88.95$,
$I_B = 73.59$, $I_c = 15.35$.

Probably the value r(O-F) = 1.41 is too high (57); the lower limit would result in values of (F) and S which are smaller by 0.216 than those given in the Appendix.

Equilibrium constants of formation have been calculated with the enthalpy of formation $\Delta Hf^{o}_{o}(OF_2) = +6.08$ k.cals. which is the most probable mean value (29).

9. Tri-fluorides of the 5th group of the periodic table, XF_3.

The ground state is $^{1}\Sigma$; point group C_{3v} (pyramidal), $P_{EO} = 1$, $S = 3$. Spectroscopic and molecular data (in general cf. 11,22,23):

Molecule	Bond Lengths	Angle FXF	Moments of Inertia	Vibrational Frequencies
NF_3	1.34	110	152.0, 79.6, 79.6	420(2), 505(1), 908(1)
PF_3	1.52	104	176, 107, 107	486(2), 531(1), 840(2), 890(1)
AsF_3	1.712 (1.72)	100	216.9, 142.8, 142.8, (220), (145), (145)	274(2), 341(1), 644(2), 707(1)
SbF_3	(1.95)	(105)		(620)
BiF_3	(2.1)	(110)		(550)

Thermodynamic functions for NF_3 have been calculated with r(N-F) = 1.34 (26). The distances r(F-N) = 1.37 or 1.45 (ref.57) would increase the values of (F) and S by 0.12 or 0.57 respectively. $\Delta H^{o}_{298.16}(NF_3) = -27.2$ k.cals. from (18) gives $\Delta Hf^{o}_{o}(NF_3) = -26.0$ k.cals. with the present data. Earlier data for PF_3 are by Stevenson and Yost (30) and our slight differences are due to the use of revised physical constants. $\Delta Hf^{o}_{o}(PF_3) = -227$ k.cals. from a comparison of bond energies. AsF_3 is 100% ionic $FAsF_2$ (31). Thermodynamic functions of AsF_3 at 298.16°K. are given in (18) which agree with our own data. $\Delta Hf^{o}_{298.16} = -218.3$ (18) gives $\Delta Hf^{o}_{o}(AsF_3) = -217$ k.cals. This value and r(AsF) = 1.712 (31) have been used in the calculations. The data for SbF_3 and BiF_3 are not adequate for thermodynamic calculations. $\Delta Hf^{o}_{o}(SbF_3) \sim -205$ k.cals.

/10.

10. Hexa-flucrides of the 6th group.

The ground state is $^1\Sigma$, point group O_h, $P_{EO} = 1$, $S = 24$; $I_A = I_B = I_C = I$. Molecular data (11,22,23,52).

Molecule	Bond Length	Moments of Inertia	Vibrational Frequencies	$-\Delta Hf^o_{298\cdot16}$	$S^o_{298\cdot16}$
SF_6	1.57	305	363(3),617(3),525(3), 645(2),775(1),965(3)	262	69.6
SeF_6	1.68	349	245(3),461(3),405(3), 662(2),708(1),787(3)	246	75.1
TeF_6	1.83	415	165(3),370(3),313(3), 674(2),701(1),752(3)	315	80.8

Meyey and Buell (51) have calculated the thermodynamic functions of SF_6 between 600 and 5000°K.: their data is fitted by:

$$C_p^o = 37.41 + 0.0876 \times 10^{-3}T - 18.78 \times 10^{-5} \times T^2$$

For the formation of SF_6 from $S_2(g)$ and $F_2(g)$ they give:

$$\Delta F^o = -271.800 - 11.33 \times T \times \ln T + 1.678 \times 10^{-3}T^2 + 9.39 \times 10^5 \times T^{-1} + 171.2 \times T$$

$$\Delta H^o = -271.100 - 11.33 \times T - 1.678 \times 10^{-3} \times T^2 + 18.78 \times 10^5 \times T^{-1}$$

Schumb (41) gives some thermochemical properties of SF_6 at low temperatures. In the above table the - ΔHf's and S's at 298.16°K. are taken from (18). The value of $S^o_{298\cdot16}$ for SF_6 compares well with the figure given in the Appendix (cf.53 for experimental values). The value C_p^o (SF_6) = 21.57 at 298.16 as given in (18) is too low and the C_p^o values from (51) agree very well with the present calculations.

11. Boron trifluoride, BF_3.

Ground state $^1\Sigma$, point group D_{3h} (plane symmetrical), $P_{EO} = 1$, $S = 6$. r(B-F) = 1.29, FBF = 120°, $I_A = 158$, $I_B = I_C = I_A/2 = 78.9$, vibrational frequencies (22,23) ω = 886, 700, 1450(2), 480(2). The thermodynamic functions (F) and S are taken from (42), the mixing term for isotopy is not included. According to (18), $\Delta Hf^o_{298\cdot16}(BF_3) = -265.4$ which gives $\Delta Hf^o_0(BF_3) = -267.0$ k.cals. and an average dissociation energy of BF bonds of ~140 k.cals. Instead of Kf^o the equilibrium constants K_p for the reaction $BF_3 \rightarrow BF + F_2$ have been calculated with ΔH = + 242 k.cals. Bibliography (57) evaluated K_p's for the reaction $BF_3 \rightarrow BF + 2F$ with ΔH = + 355.0 k.cals. whereas our new ΔHf values lead to ΔH = + 282 k.cals.

/12.

12. Chlorine trifluoride, ClF_3.

The molecular ground state is assumed to be $^1\Sigma$ with $P_{EO} = 1$. Recently (21) the infra-red and Raman-spectra of ClF_3 have been investigated but no analysis was made in view of the complex character of the bands due partly to molecular association in the liquid phase (9, 21). Another spectroscopic investigation (32) gives the following information:-

$\omega_1 = 508$; $\omega_{2,4} = 750$, $\omega_{3,5} = 316$; $\omega_4 = 428$; mean moment of inertia

$\bar{I} = 130$ with an estimated error of about 10% .

These frequencies were used in calculating the thermodynamic functions of ClF_3. A pyramidal C_{3v} structure was assumed in agreement with the appearance of 4 Raman active frequencies and the existence of the dimer - possibly $F_3Cl\text{-}ClF_3$ (with contributions from $F_3\overset{+}{Cl}\text{-}ClF_3^-$) in agreement with the low heat of polymerisation (33). The angle $F\hat{Cl}F$ was assumed $\sim 110^\circ$ and $r_0(Cl\text{-}F) = 1.63$ i.e. the same as in ClF, although this leads to the rather high moments of inertia $I_A = 225$, $I_B = I_C = 122.5$, $\bar{I} = 150$.

The following values have been quoted for the heat of formation of ClF_3 at 298.16°K: -42.0 ± 1.5 (33), -37.1 (32), -28.4 k.cals. (27). The mean value $Hf^\circ_0(ClF_3) = -36$ k.cals. was used for calculating equilibrium constants.

13. Silicon tetra-fluoride, SiF_4.

The ground state is $^1\Sigma$; point group T_d, $P_{EO} = 1$, $S = 12$. Tetrahedral angles $F\hat{Si}F = 109^\circ\,28'$ and nuclear distances $r_0(Si\text{-}F) = 1.54$ (39) give the moments of inertia $I_A = I_B = I_C = (8/3)(M_F/N) = 199.5$ (N = Avogadro number). The vibrational frequencies (22, 23) are:- $\omega = 800$, 260(2), 1022(3), 420(3). Earlier values (18, 40) of S at 298.16°K. are somewhat higher than our value. It is not known whether these earlier values include the mixing term $S_{mix} = 0.304$, which is not contained in the figures given in the Appendix. In calculating the equilibrium constants $\Delta Hf^\circ_0(SiF_4) = -373$ k.cals. has been used (cf. $\Delta Hf^\circ_{298.16} = -370$ k.cals in (18).

14. Carbon tetra-fluoride, CF_4.

The ground state is $^1\Sigma$, point group T_d, $P_{EO} = 1$, $S = 12$. No upper states need be considered because of the absence of absorption in the near ultra-violet.

Tetrahedral angles $F\hat{C}F = 109^\circ\,28'$ and bond distances $r(C\text{-}F) = 1.36$ give the moments of inertia $I_A = I_B = I_C = 154.8$. The vibrational frequencies (22,23) are:- $\omega = 904$, 437(2), 1265(3), 630(3) (cf.34 for force constants). The C-F bonds are mainly covalent but there is some resonance with $\overset{-+}{FCF_3}$ (24). The enthalpy of formation has been amended from -164 (11,18) to $\Delta Hf^\circ_{300}(CF_4) = -231 \pm 3$ k.cals. (27) and this value has been used as ΔHf°_0 in calculating the equilibrium constants. The entropy figure at

/300°K.

300°K. agrees well with that given in (18).

15. Carbon-oxyfluoride, COF_2.

The most probable structure is $^1\Sigma$; point group C_{2v}, with $P_{EO} = 1$ and $S = 2$ as in $COCl_2$ and $COBr_2$. $F\hat{C}F = 115°$ $r_o(C\text{-}O) = 1.27$ and $r_o(C\text{-}F) = 1.38$ have been assumed and these give $I_A = 75.89$, $I_B = 85.47$, $I_C = I_A + I_B = 161.45$. It may well be that r(C-F) is as small as ~1.32 or even smaller, as is suggested by comparing r(C-X) in the series COX_2, (X = Cl, Br) with the normal bond length r(C-X). As this procedure is open to criticism the average r(C-F) = 1.38 has been preferred.

Recently (35) infra-red and Raman bands of COF_2 have been communicated but no analysis was made. The following six frequencies have been used in the calculations, $\omega = 580, 626, 775, 965, 1249, 1941$ cm^{-1}. The enthalpy of formation was taken as $\Delta Hf^o_o(COF_2) = -150$ k.cals. in good agreement with the experimental value of (27). This corresponds roughly to the same value D(C-O) ~ 158 k.cals. in COF_2 and $COCl_2$ calculated from average bond energies.

16. Hexafluoroethane, C_2F_6.

The structure is either staggered D_{3d} or eclipsed D_{3h} both having the symmetry number S = 6.

The vibrational frequencies and their assignment are (36) $\omega_1 = 1420$, $\omega_2 = 809$, $\omega_3 = 349$, $_5 = 1117$, $\omega_6 = 714$, $\omega_7 = 1250(2)$, $\omega_8 = 523(2)$, $\omega_9 = 216(2)$, $\omega_{10} = 1237(2)$, $\omega_{11} = 620(2)$, $\omega_{12} = 380(2)$: (force constants cf. 34). The torsional frequency ω_4 is not known, since it is inactive in both infra-red and Raman spectrum.

Unfortunately the bond distances are not known with accuracy. The normal distances r(C-C) = 1.54 and r(C-F) = 1.36 (24) have been found to give vibrational frequencies for the Urey-Bradley field which agree well with the experimental ones (46). This method, however, does not include the interaction of the two CF_3 groups. According to (47) the distances r(C-C) = 1.45 (37) and r(C-F) = 1.35 are not in very good agreement with magnetic measurements on the solid crystal. An even smaller r(C-F) (48) would however improve this situation.

Tetrahedral angles $F\hat{C}F = 109° \, 28'$ have been assumed, r(C-F) = 1.35, r(C-C) = 1.45 in agreement with (37), giving $I_A = 306.7$, $I_B = I_C = 435.5$. The normal values of r(C-C) = 1.54, r(C-F) = 1.36 would give (36), $I_A = 311.2$, $I_B = I_C = 462.4$, whereas a Gerhard & Dennison extrapolation of measurements on the Q, P and R branches give $I_A = 98$, $I_B = I_C = 401$ which are obviously too low.

The contribution from the internal movement about the C-C axis depends on whether this movement is a torsional oscillation or a free or hindered internal rotation. Since no spectroscopic nor calorimetric measurements are available we can only estimate this contribution. It will be assumed that there is an internal rotation restricted by a potential barrier of estimated height V ~3500 cals. The reduced moment of inertia in internal rotation is $I_r = I_A/4$ ~76.7 and the symmetry number S = 3, corresponding to 3 equivalent positions of the two CF_3 groups relative to each other. With n = 3 equal and equidistant maxima, the potential V ~3.5 k.cals. corresponds to the torsional frequency $\omega_r = (n/2\pi)(V/2I_r)^{\frac{1}{2}}$ ~75 cm^{-1}. In the

/following

following table (cf. Appendix 3, Sec. VIII) the contributions from this frequency (v) are compared with those for free (f) and restricted (r) internal rotation, the latter increments being calculated from Pitzer's tables (cf. 51) with V = 3500, and $10^{-36} \times n^2/I_r V = 0.335$.

As an approximation the problem is treated as an equilibrium between the oscillating staggered D_{3d} form, which also occurs in the similar C_2Cl_6 molecule (38), and the form having restricted internal rotation, viz:-

$$C_2F_6(D_{3d}, osc.) \rightleftharpoons C_2F_6(rot.);\; K \equiv [C_2F_6(rot.)] / [C_2F_6(osc.)] \equiv X/(I-X);$$

$$X \equiv [C_2F_6(rot.)] = K/(K+1) \text{ and}$$

$$R\ln K = (F)r - (F)v - \Delta H^o_o/T;\quad \Delta H^o_o = V/2 - \omega_r/2 = 1650 \text{ cals.}$$

The corresponding values of K and X are listed in the last column of Table 3. The thermodynamic functions of C_2F_6 in the Appendix have been obtained by combining the functions of the two forms according to their molar fractions. In view of the general uncertainty of the other data this procedure was thought satisfactory, although, strictly speaking in the transitional region one ought to calculate (F) etc. from the partition function with eigen values of E_r from the wave-equation (Mathieu equation).

The old value of $\Delta Hf(C_2F_6)$ = 240 k.cals. (18) is definitely wrong. With the new $\Delta Hf^o_o(CF_4)$ = -231 k.cals. the approximate value $\Delta Hf^o_o(C_2F_6)$ = -315 k.cals. was derived by using average bond energies D(C-F) = 107, and D(C-C) = 67 k.cals. according to the shorter bond in C_2F_6.

V. DISCUSSION OF RESULTS.

1. The equilibrium constants Kf^o of formation of F and HF replace earlier erroneous data (60). F_2 and HF are more dissociated at high temperature than previously assumed. Above 1500-2000°K. fluorine should behave as a monatomic gas.

2. The final reaction temperature of the process

$$\tfrac{1}{2}Cl_2 + \tfrac{1}{2}F_2 \rightleftharpoons ClF$$

which was used (20) to determine $\Delta Hf(FCl)$, is 1660 or 2080°K. depending on whether $\Delta Hf^o(FCl)$ = -11.6 or -15.0 k.cals. respectively. At the higher temperature dissociation of FCl into atoms amounts to ~2 per cent at 1 atm. pressure.

3. Apart from dissociation, the formation of ClF_3 may have influenced Wicke's (20) measurement of $\Delta Hf^o(FCl)$ to an even larger extent, especially if $-\Delta Hf(ClF_3)$ is larger than +36 k.cals., the figure accepted. From this it appears that $-\Delta Hf^o(ClF)$ = +11.6 may be slightly too low.

4. At temperatures below 800-900°K. the formation of NF_3 is thermodynamically possible. Apparently kinetic conditions are unfavourable, an obstacle, however which might be overcome as in the synthesis of ammonia.

/5.

5. CF_4 and COF_2 are formed easily from F_2 and either C (solid) or CO. Under comparable conditions CF_4 is the major product.

6. The equilibrium constants for the reactions:-

$$CO + 2HF \rightleftharpoons COF_2 + H_2 ; \quad \Delta H_0^o = +6.20 \text{ k.cals.}$$

$$COF_2 + 2HF \rightleftharpoons CF_4 + H_2O; \quad \Delta H_0^o = -9.11 \text{ k.cals.}$$

$$CF_4 + 2H_2O \rightleftharpoons CO_2 + 4HF; \quad \Delta H_0^o = -6.76 \text{ k.cals.}$$

$$COF_2 + H_2O \rightleftharpoons CO_2 + 2HF; \quad \Delta H_0^o = -15.86 \text{ k.cals.}$$

are given in the Appendix; these equilibria correspond to the water-gas equilibrium in the oxidation of hydrocarbons.

7. Both the equilibria

$$C_{solid} + 4HF \rightarrow CF_4 + 2H_2; \quad \Delta H_0^o = +27.0 \text{ k.cals.}$$

and

$$C_{solid} + F_2O \rightarrow CO + F_2 \rightarrow COF_2; \ \Delta H_0^o = -33.28 \text{ and } -156 \text{ k.cals.resp.}$$

behave rather differently from the corresponding reaction

$$C_{solid} + H_2O \rightarrow CO + H_2 \rightarrow H_2CO.$$

8. The equilibrium constants for the reaction

$$2CF_4 \rightleftharpoons C_2F_6 + F_2; \quad \Delta H_0^o \sim +147 \text{ k.cals.}$$

show that this reaction occurs to a very small extent in comparison with the hydrocarbons.

9. The special behaviour of most of the equilibria under (6) and (7) together with those of the reactions

$$CF_4 + O_2 \rightleftharpoons CO_2 + 2F_2; \quad \Delta H_0^o = +137.03 \text{ k.cals.}$$

$$CF_4 + \tfrac{1}{2}O_2 \rightleftharpoons CO + 2F_2 ; \quad \Delta H_0^o = +203.80 \text{ k.cals.}$$

might explain some of the peculiarities of the combustion of organic fluorine compounds. As a practical result it can be concluded that the lower perfluorinated paraffins are reasonably stable to dry oxygen up to fairly high temperatures but may react with H_2 or H_2O.

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$T^\circ K.$	F: $-(F^\circ-H^\circ_o)/T$	F: S°	F: C°_p	F: log Kf for Hf° = +20	F: log Kf for Hf° = +16.2	F: Kf° for Hf° +20	F: Kf° for Hf° +16.2	F_2: $-(F^\circ-H^\circ_o)/T$	F_2: S°	F_2: C°_p	HF: $-(F^\circ-H^\circ_o)/T$	HF: S°	HF: C°_p	HF: log Kf°	HF: Kf°
298.16	32.692	37.917	5.435					41.44			34.60		6.955		
300	32.723	37.950	5.434	-11.951	-9.183	1.12×10^{-12}	6.56×10^{-10}	41.48			34.64		6.955	47.352	2.25×10^{47}
400	34.234	39.504	5.361	- 8.200	-6.124	6.31×10^{-9}	7.52×10^{-7}	43.51	50.64	7.610	36.62		6.955	35.602	4.00×10^{35}
500	35.412	40.692	5.282	- 5.933	-4.272	1.17×10^{-6}	5.35×10^{-5}	45.12	52.37	7.91	38.15	45.10	6.96	28.547	3.51×10^{28}
600	36.374	41.650	5.218	- 4.411	-3.027	3.88×10^{-5}	9.40×10^{-4}	46.45	53.83	8.14	39.42	46.37	6.97	23.842	6.95×10^{23}
800	37.948	43.198	[illegible]	- 2.482	-1.443	3.30×10^{-3}	3.61×10^{-2}	48.61	56.21	8.43	41.42	48.38	7.03	17.953	8.98×10^{17}
1000	39.057	44.278	5.083	- 1.334	-0.504	4.66×10^{-2}	3.14×10^{-1}	50.32	58.11	8.59	42.98	49.96	7.16	14.413	2.59×10^{14}
1200	40.006	45.201	5.052	- 0.555	0.137	2.79×10^{-1}	1.37	51.76	59.69	8.69	44.25	51.28	7.33	12.045	1.11×10^{12}
1400	40.805	45.978	5.032	0.006	0.599	1.01	3.97	52.99	61.03	8.75	45.34	52.43	7.51	10.352	2.25×10^{10}
1500	41.162	46.325	5.025	0.231	0.785	1.70	6.09	53.55	61.64	8.78	45.83	52.95	7.60	9.674	4.72×10^{9}
1600	41.494	46.648	5.018	0.429	0.948	2.68	8.86	54.07	62.20	8.80	46.29	53.44	7.69	9.079	1.20×10^{9}
1800	42.101	47.240	5.008	0.759	1.221	5.74	1.66×10^{1}	55.03	63.25	8.83	47.14	54.36	7.84	8.088	1.22×10^{8}
2000	42.641	47.767	5.001	1.025	1.440	1.06×10^{1}	2.75×10^{1}	55.90	64.18	8.85	47.91	55.19	7.99	7.294	1.97×10^{7}

$T^\circ K.$	ClF: $-(F-H^\circ_c)/T$	ClF: S°	ClF: C°_p	ClF: log Kf for Hf° = -15.0	ClF: log Kf for Hf° = -11.6	ClF: Kf° for Hf° -15.0	ClF: Kf° for Hf° -11.6	BeF: $-(F^\circ-H^\circ_o)/T$	BeF: S°	BeF: C°_p	BrF: $-(F^\circ-H^\circ_o)/T$	BrF: S°	BrF: C°_p	BrF: log Kf°	BrF: Kf°
298.16	44.90	52.05	7.672					42.14	49.12		47.65	54.89	7.850		
300	44.95	52.09	7.680	11.194	8.718	1.56×10^{11}	5.22×10^{8}	42.18	49.16	7.125	47.70	54.93	7.861	5.868	7.39×10^{5}
400	47.03	54.36	8.072	8.460	6.603	2.88×10^{8}	4.00×10^{6}	44.20	51.25	7.399	49.81	57.24	8.215	4.474	2.98×10^{4}
500	48.68	56.19	8.35	6.820	5.33	6.61×10^{6}	2.16×10^{5}	45.78	52.93	7.68	51.49	59.10	8.43	3.637	4.34×10^{3}
600	50.07	57.73	8.53	5.727	4.49	5.33×10^{5}	3.08×10^{4}	47.10	54.36	7.93	52.89	60.66	8.57	3.080	1.20×10^{3}
800	52.31	60.22	8.76	4.362	3.43	2.30×10^{4}	2.71×10^{3}	49.21	56.69	8.27	55.16	63.14	8.72	2.384	2.42×10^{2}
1000	54.09	62.19	8.89	3.545	2.86	3.51×10^{3}	6.33×10^{2}	50.90	58.56	8.47	56.96	65.10	8.80	1.961	9.26×10^{1}
1200	55.59	63.82	8.98	3.001	2.38	1.00×10^{3}	2.41×10^{2}	52.31	60.11	8.60	58.45	66.71	8.84	1.688	4.88×10^{1}
1400	56.86	65.21	9.05	2.612	2.08	4.09×10^{2}	1.21×10^{2}	53.52	61.45	8.68	59.73	68.07	8.87	1.490	3.09×10^{1}
1500	57.44	65.84	9.08					54.07	62.05	8.72	60.31	68.69	8.88		
1600	57.99	66.43	9.11					54.59	62.61	8.74	60.85	69.25	8.89		
1800	58.98	67.50	9.16					55.54	63.64	8.78	61.84	70.31	8.90		
2000	59.89	68.47	9.20	(1.866)		(7.35 x 10)		56.40	64.57	8.81	62.73	71.24	8.91		

TABLES OF THERMODYNAMIC FUNCTIONS (Contd.)

$T^oK.$	CF_2 $-(F^o-H^o_o)/T$	S^o	C^o_p	log Kf^o	Kf^o	NF_3 $-(F^o-H^o_o)/T$	S^o	C^o_p	log Kf^o	Kf^o	BF $-(F^o-H^o_o)/T$	S^o	C^o_p
298.16	50.31	58.93	10.08			53.16	63.07				41.02	48.0	
300	50.36	59.00	10.10	-7.090	8.13×10^{-8}	53.21	63.13	13.32	12.725	5.31×10^{12}	41.06	48.03	7.064
400	52.91	62.04	11.08	-6.088	8.16×10^{-7}	56.21	67.22	15.12	7.761	5.77×10^{7}	43.07	50.09	7.287
500	55.00	64.60	11.79	-5.488	3.25×10^{-6}	58.77	70.74	16.37	4.784	6.08×10^{4}	44.64	51.74	7.55
600	56.79	66.79	12.29	-5.687	8.18×10^{-6}	61.03	73.81	17.23	2.807	6.41×10^{2}	45.95	53.14	7.79
800	59.76	70.42	12.90	-4.582	2.12×10^{-5}	64.89	78.91	18.24	0.355	2.26	48.04	55.44	8.16
1000	62.20	73.34	13.23	-4.279	5.34×10^{-5}	68.00	82.93	18.76	-1.123	7.52×10^{-2}	49.71	57.28	8.39
1200	64.26	75.77	13.42	-4.665	8.61×10^{-5}	70.90	86.50	19.09	-2.051	8.89×10^{-3}	51.11	58.83	8.54
1400	66.06	77.85	13.54	-3.914	1.22×10^{-4}	73.35	89.46	19.29	-2.721	1.90×10^{-3}	52.31	60.15	8.63
1500	66.88	78.79	13.58	-3.861	1.41×10^{-4}	74.47	90.80	19.36	-2.985	1.04×10^{-3}	52.85	60.75	8.67
1600						75.51	92.03	19.42	-3.218	6.05×10^{-4}	53.36	61.31	8.70
1800						77.47	94.31	19.51	-3.708	1.96×10^{-4}	54.30	62.33	8.75
2000						79.27	96.39	19.58	-3.893	1.28×10^{-4}	55.15	63.26	8.78

$T^oK.$	ClF_3 $-(F^o-H^o_o)/T$	S^o	C^o_p	log Kf^o	Kf^o	SiF_4 $-(F^o-H^o_o)/T$	S^o	C^o_p	log Kf^o	Kf^o	BF_3 $-(F^o-H^o_o)/T$	S^o	C^o_p
298.16						55.11	67.30				54.39	64.17	
300	55.95	67.02	15.34	19.832	6.79×10^{19}	55.16	67.35	17.48	265.231	1.70×10^{265}	54.44	64.22	13.43
400	59.32	71.67	16.88	13.110	1.29×10^{13}	58.90	72.71	19.78	197.046	1.11×10^{197}	57.41	68.37	15.38
500	62.19	75.54	17.79	9.090	1.23×10^{9}	62.13	77.31	21.37	156.126	1.34×10^{156}	59.97	71.95	16.65
600	64.70	78.84	18.36	6.422	2.64×10^{6}	65.01	81.31	22.45	128.842	7.03×10^{128}	62.24	75.07	17.48
800	68.93	84.21	18.95	3.109	1.29×10^{3}	69.94	87.96	23.75	94.751	5.64×10^{94}	66.12	80.25	18.43
1000	72.43	88.48	19.28	1.143	1.39×10^{1}	74.10	93.34	24.43	74.300	2.00×10^{74}	69.37	84.42	18.92
1200	75.41	92.02	19.46	-0.153	7.03×10^{-1}	77.69	97.82	24.84	60.672	4.70×10^{60}	72.17	87.88	19.20
1400	77.99	95.02	19.56	-1.071	8.49×10^{-2}	80.85	101.68	25.09	50.946	8.83×10^{50}	74.64	90.86	19.37
1500	79.17	96.31	19.60			82.31	103.43	25.18	47.058	1.14×10^{47}	75.77	92.21	19.43
1600	80.30	97.65	19.63			83.67	105.04	25.26	43.639	4.36×10^{43}	76.83	93.45	19.48
1800	82.35	99.95	19.68			86.25	108.06	25.37	37.984	9.64×10^{37}	78.81	95.76	19.56
2000	84.22	102.03	19.72			88.53	110.70	25.46	33.466	2.92×10^{33}	80.63	97.85	19.62

TABLES OF THERMODYNAMIC FUNCTIONS (Contd.)

	CF_4				COF_2					AsF_3		
$T^oK.$	$-(F^o-H^o_o)/T$	S^o	C^o_p	log Kf^o	$-(F^o-H^o_o)/t$	S^o	C^o_p	log Kf^o	Kf^o	$-(F^o-H^o_o)/T$	S^o	C^o_p
298.16										57.64	69.10	
300	52.48	62.72	14.67	161.504	53.37	62.30	11.34	107.155	1.43×10^{107}	57.69	69.16	15.71
400	55.63	67.33	17.36	119.168	56.05	65.81	13.10	79.694	4.94×10^{79}	61.17	73.90	17.15
500	58.39	71.43	19.35	93.889	58.32	68.89	14.46	63.207	1.61×10^{63}	64.12	77.83	17.99
600	60.87	75.10	20.80	76.818	60.31	71.62	15.50	52.211	1.63×10^{52}	66.69	81.16	18.51
800	65.24	81.36	22.63	55.651	63.74	76.29	16.92	38.459	2.88×10^{38}	71.01	86.56	19.07
1000	68.99	86.52	23.65	42.960	66.65	80.17	17.78	30.205	1.60×10^{30}	74.56	93.32	19.35
1200	72.30	90.90	24.26	34.513	69.18	83.46	18.33	24.701	5.02×10^{24}	77.58	96.86	19.50
1400	75.20	94.68	24.65	28.478	71.44	86.32	18.69	20.769	5.87×10^{20}	80.21	99.88	19.60
1500	76.58	96.38	24.80	26.074	72.47	87.61	18.83	19.197	1.57×10^{19}	81.39	101.23	19.63
1600	77.83	97.94	24.92	23.962	73.45	88.83	18.94	17.822	6.64×10^{17}	82.52	102.50	19.66
1800	80.29	100.94	25.10	20.464	75.29	91.07	19.12	15.526	3.36×10^{15}	84.60	104.82	19.70
2000	82.47	103.67	25.23	17.660	76.96	93.08	19.26	13.690	4.90×10^{13}	86.48	106.90	19.73

	C_2F_6					BF_3			SF_6			
$T^oK.$	$-(F^o-H^o_o)/T$	S^o	C^o_p	log Kf^o	Kf^o	$-(F^o-H^o_o)/T$	S^o	C^o_p	$-(F^o-H^o_o)/T$	S^o	C^o_p	
298.16						51.34	60.69		55.98	69.41	22.91	
300	63.0	79.2	25.2	215.8	6×10^{215}	51.39	60.74	12.10	56.04	69.52	23.09	
400	68.1	87.1	29.5	158.1	10^{151}	54.21	64.45	13.77	60.34	76.83	27.65	
500	72.6	94.1	32.8	123.5	3×10^{123}	56.59	67.87	14.97	64.30	83.34	30.55	
600	76.7	100.3	35.2	100.4	3×10^{100}	58.69	70.51	16.05	67.96	89.09	32.42	
800	84.1	112.2	38.1	71.61	4×10^{71}	62.26	75.33	17.36	74.50	98.75	34.54	
1000	90.4	119.7	39.8	54.40	2×10^{54}	65.29	79.30	18.13	80.15	106.57	35.62	
1200	96.0	127.0	40.8	42.94	9×10^{42}	67.91	82.64	18.61	85.11	113.13	36.25	
1400	100.8	133.4	41.4	34.75	6×10^{34}	70.22	85.53	18.92	89.53	118.75	36.64	
1500	103.1	136.3	41.6	31.49	3×10^{31}	71.29	86.84	19.03	91.62	121.34	36.78	
1600	105.3	139.0	41.8	28.65	4×10^{28}	72.30	88.07	19.12	93.49	123.65	36.89	
1800	109.4	143.9	42.2	23.93	9×10^{23}	74.18	90.33	19.27	97.17	128.09	37.07	
2000	113.1	148.4	42.4	20.14	1×10^{20}	75.9	92.37	19.38	100.35	131.89	37.19	

TABLES 2 - EQUILIBRIUM CONSTANTS

Reaction	$BF_3 \rightleftharpoons BF + F_2$		$ClF + F_2 \rightleftharpoons ClF_3$		$CO + 2F_2 \rightleftharpoons CF_4 + \frac{1}{2}O_2$		$CO_2 + 2F_2 \rightleftharpoons CF_4 + O_2$		$2COF_2 \rightleftharpoons CF_4 + CO_2$	
Equilibrium Constant K_p	$\frac{P_{BF} \cdot P_{F_2}}{P_{BF_3}}$		$\frac{P_{ClF} \cdot P_{F_2}}{P_{ClF_3}}$		$\frac{P_{CF_4} \cdot P_{O_2}^{\frac{1}{2}}}{P_{CO} \cdot P_{F_2}^2}$		$\frac{P_{CF_4} \cdot P_{O_2}}{P_{CO_2} \cdot P_{F_2}^2}$		$\frac{P_{CF_4} \cdot P_{CO_2}}{P_{COF_2}^2}$	
Enthalpy of Reaction ΔH_o^c	- 242		- 24		- 203.80		- 137.03		- 24.97	
$T^oK.$	log K_p	K_p	log K_p	K_p	log K_p	K_p	log K_p	K_p	log K_p	K_p
300	-169.487	3.26×10^{-170}	10.823	6.65×10^{10}	135.576	3.77×10^{137}	88.466	2.92×10^{88}	15.860	7.24×10^{15}
400	-125.145	7.16×10^{-126}	6.289	1.94×10^{6}	100.041	1.10×10^{100}	67.632	4.29×10^{67}	11.315	2.07×10^{11}
500	- 98.527	2.97×10^{-99}	3.581	3.81×10^{3}	77.505	3.20×10^{77}	52.500	3.16×10^{52}	8.601	3.99×10^{8}
600	- 80.780	1.66×10^{-81}	1.787	6.12×10^{1}	62.482	3.03×10^{62}	42.417	2.61×10^{42}	6.799	6.30×10^{6}
800	- 58.595	2.54×10^{-59}	-0.434	3.68×10^{-1}	43.719	5.24×10^{43}	29.824	6.67×10^{29}	4.559	3.62×10^{4}
1000	- 45.294	5.08×10^{-46}	-1.746	1.79×10^{-2}	32.483	3.04×10^{32}	22.284	1.92×10^{22}	3.227	1.69×10^{3}
1200	- 36.448	3.56×10^{-37}	-2.608	2.47×10^{-3}	25.014	1.03×10^{25}	17.273	1.87×10^{17}	2.351	2.24×10^{2}
1400	- 30.113	7.71×10^{-31}	-3.216	6.08×10^{-4}	19.688	4.88×10^{19}	13.696	4.97×10^{13}	1.720	5.25×10^{1}
1500	- 27.587	2.59×10^{-28}	-3.455	3.51×10^{-4}	17.569	3.71×10^{17}	12.275	1.88×10^{12}	1.479	3.01×10^{1}
1600	- 25.378	4.19×10^{-26}	-3.661	2.18×10^{-4}	15.709	5.12×10^{15}	11.023	1.05×10^{11}	1.258	1.81×10^{1}
1800	- 21.700	2.0×10^{-22}	-4.005	9.89×10^{-5}	12.635	4.32×10^{12}	8.964	9.20×10^{8}	0.912	8.17
2000	- 18.762	1.73×10^{-19}	-4.276	5.30×10^{-5}	10.171	1.48×10^{10}	7.307	2.03×10^{7}	0.628	4.25

TABLES 2 - EQUILIBRIUM CONSTANTS (Contd.)

Reaction	$COF_2 + 2HF \rightleftharpoons CF_4 + H_2O$		$CO + 2HF \rightleftharpoons COF_2 + H_2$		$CF_4 + 2H_2O \rightleftharpoons CO_2 + 4HF$		$COF_2 + H_2O \rightleftharpoons CO_2 + 2HF$		$CF_4 + 2H_2 \rightleftharpoons (C) + 4HF$		$2CF_4 \rightleftharpoons C_2F_6 + F_2$	
Equilibrium Constant K_p	$\frac{P_{CF_4}\cdot P_{H_2O}}{P_{COF_2}\cdot P^2_{HF}}$		$\frac{P_{COF_2}\cdot P_{H_2}}{P_{CO}\cdot P^2_{HF}}$		$\frac{P_{CO_2}\cdot P^4_{HF}}{P_{CF_4}\cdot P^2_{H_2O}}$		$\frac{P_{CO_2}\cdot P^2_{HF}}{P_{COF_2}\cdot P_{H_2O}}$		$\frac{P^4_{HF}}{P_{CF_4}\cdot P^2_{H_2}}$		$\frac{P_{C_2F_6}\times P_{F_2}}{P^2_{CF_4}}$	
Enthalpy of Reaction ΔH^o_c	- 9.11		+ 6.20		- 6.76		- 15.86		- 27.0		+ 147	
T^o K.	log K_p	K_p	log K_p	K_p	log K_p	K_p	log K_p	K_p	log K_p	K_p	log K_p	K_p
300	-0.566	2.71×10^{-1}	-11.476	3.34×10^{-12}	16.993	9.84×10^{16}	16.427	2.67×10^{16}	27.902	7.98×10^{27}	-107.2	6×10^{-108}
400	-2.489	3.24×10^{-3}	-10.635	2.32×10^{-11}	16.293	1.96×10^{16}	13.804	6.37×10^{13}	23.238	1.73×10^{23}	- 80.23	6×10^{-81}
500	-3.655	2.21×10^{-4}	-10.137	7.29×10^{-11}	15.910	8.13×10^{15}	12.256	1.80×10^{12}	20.425	2.66×10^{20}	- 64.06	9×10^{-65}
600	-4.444	3.60×10^{-5}	- 9.809	1.55×10^{-10}	15.466	2.92×10^{15}	11.240	1.74×10^{11}	18.550	3.55×10^{18}	- 53.24	6×10^{-54}
800	-5.426	3.75×10^{-6}	- 9.380	4.17×10^{-10}	15.411	2.58×10^{15}	9.985	9.66×10^{9}	16.163	1.46×10^{16}	- 39.31	5×10^{-40}
1000	-6.009	9.79×10^{-7}	- 9.098	7.98×10^{-10}	15.245	1.76×10^{15}	9.236	1.72×10^{9}	14.692	4.92×10^{14}	- 31.54	3×10^{-32}
1200	-6.380	4.17×10^{-7}	- 8.888	1.29×10^{-9}	15.110	1.29×10^{15}	8.731	5.38×10^{8}	13.669	4.67×10^{13}	- 26.07	9×10^{-27}
1400	-6.648	2.25×10^{-7}	- 8.725	1.88×10^{-9}	15.017	1.04×10^{15}	8.369	2.34×10^{8}	12.931	8.53×10^{12}	- 22.20	6×10^{-23}
1500	-6.744	1.80×10^{-7}	- 8.655	2.21×10^{-9}	14.966	9.25×10^{14}	8.223	1.67×10^{8}	12.620	4.17×10^{12}	- 20.7	2×10^{-21}
1600	-6.843	1.44×10^{-7}	- 8.590	2.57×10^{-9}	14.943	8.77×10^{14}	8.101	1.26×10^{8}	12.354	2.26×10^{12}	- 19.3	5×10^{-20}
1800	-6.975	1.06×10^{-7}	- 8.479	3.32×10^{-9}	14.862	7.28×10^{14}	7.887	7.71×10^{7}	11.887	7.71×10^{11}	- 17.0	10^{-17}
2000	-7.090	8.14×10^{-8}	- 8.385	4.12×10^{-9}	14.808	6.43×10^{14}	7.716	5.22×10^{7}	11.518	3.30×10^{11}	- 15.2	6×10^{-16}

TABLE 3 - CONTRIBUTIONS FROM INTERNAL MOVEMENT IN C_2H_6 ABOUT C-C AXIS

$T^oK.$	Free Energy Function			Energy Function			Entropy			Heat Capacity			Equilibrium	
	(F)v	(F)f	(F)rr	(E)v	(E)f	(E)rr	Sv	Sf	Srr	Cv	Cf	Crr	log K	x
300	2.379	5.262	2.73	1.651	0.994	3.00	4.03	6.256	4.65	1.966	0.994	2.31	-1.126	0.069
400	2.871	5.548	3.27	1.732	0.994	2.00	4.60	6.542	5.31	1.975	0.994	2.30	-0.813	0.13
500	3.257	5.770	3.75	1.780	0.994	2.08	5.04	6.764	5.80	1.979	0.994	2.21	-0.614	0.19
1000	4.530	6.458	5.16	1.881	0.994	1.88	6.41	7.452	7.12	1.985	0.994	1.56	-0.223	0.38
2000	5.857	7.147	6.42	1.934	0.994		7.79	8.141	8.05	1.987	0.994	1.17	-0.06	0.46

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